Statistical preparation and characterization of Bi-based superconducting thin films

E. Díaz-Valdés
Escuela Superior de Física y Matemáticas - I.P.N., Edif 9 UPALM, México D.F. 07738, México

M. Jergel, C. Falcony-Guajardo
Centro de Investigación y Estudios Avanzados - I.P.N., A.P. 14-740, México, D.F. 07000, México

F. Morales
Instituto de Investigaciones en Materiales, UNAM, A.P. 70-360, México D.F. 04510, México

J. Araujo-Osorio
Escuela Superior de Ingeniería Química e Industrias Extractivas-IPN, Edif. 7 UPALM, México D.F. 07738, México

Bi-Pb-Sr-Ca-Cu-O/MgO thin films were prepared by deposition of an aerosol from aqueous nitrate solutions. To prepare the samples, an experimental design was applied to investigate the influence of nine different variables upon synthesis of superconducting phases. Within this design, the influence of chemical composition of the nitrate solutions and the precursor thermal treatment upon formation of superconducting phases were studied. The T_c values of the samples were used as a quantitative parameter to analyze and optimize various parameters studied in the film preparation. The analysis revealed a significant influence of the Bi and/or Bi/Pb content as well as that of Cu and thermal treatment parameters. Results from XRD, SEM, EDS and T_c measurements showed correlation between the film preparation conditions, film chemical composition and the formation of superconducting phases.
Keywords: Superconducting Bi-based films, film processing, film properties, experimental design.

1. Introduction

Since the discovery of the bismuth-based superconductors [1,2], a variety of applications of bulk material [3] as well as thin films [4-8] have been reported. Bi-based films are already used in low current as well as power (transmission lines) applications. Currently, several physical [4-6] and chemical techniques [7,8] are being used for their preparation. It has been found that the nominal composition and thermal treatment parameters such as heating-up rate, annealing temperature, annealing time, and cooling rate play an important role in the formation of high-T_c phases [8,9]. It is also known that the addition of Pb, together with an appropriate fabrication process increases the content of high-T_c phases and the thermodynamical stability of these phases [2,6,7]. Influence of the Bi content upon the critical temperature T_c values, the *c*-axis lattice parameter and the surface morphology of the synthesized films [5] is also recognized. A cooling rate following the sintering of a sample is another parameter, which has been found to affect the growth of the high-T_c phases. It has been reported [4] that by rapid cooling it is possible to grow an almost single-phase 110 K film. Other variable in the processing of superconducting materials is the content of oxygen that can be introduced by keeping its constant partial pressure during the thermal treatment or by chemical reaction as in our case. In the BSCCO system, in comparison to the YBCO one, the change in T_c in relation with the oxygen content has been found to be much less dependent [10]. To grow Bi-based superconducting films, different types of monocrystalline substrates such as yttrium stabilized zirconia (YSZ), $SrTiO_3$, BeO, $LaAlO_3$ and/or MgO (001) have been used up to now by various authors. From the point of view of their lattice parameters, thermal expantion coefficients and the best electrical properties of the synthesized Bi-based films, the $SrTiO_3$, $LaAlO_3$ and the MgO (001) substrates seems to be as most suitable ones [4-6,8]. Taking into consideration also the cost of these substrates, we selected the MgO (001) for the present experimental work.

When growing the Bi-based films, many technological parameters are involved in such a process, influencing the final properties of the synthesized films. In this work we investigated an influence of the most important ones. The value of each of investigated parameters may be varied only within a particular interval, limited by its minimum and maximum value. In order to minimize and to optimize the number of experiments needed for investigation of influence of each of these particular factors, we considered for our experimental design only these two values. We presume that such a change of investigated parameter depends from the change in value of the rest of participating factors. Applying a statistical experimental design allow us not only to know the importance of individual participated factors involved in the process, but also to quantify their influence upon the response ($T_{c,on}$ values). The general characteristic of experimental designs of this type is that more than one parameter is changed in each experimental run as to limit the number of experiments performed (in our particular case we changed at the same time 9 parameters).

The presented experiment consists of 16 trials, with the aim of evaluating nine processing factors affecting the superconducting and physical properties of the films. The effect of the factors at two levels (high and low values inside of an interval of the corresponding factor) on the film properties could be efficiently identified using a fractional factorial design 2_{III}^{9-5} which allowed fast, economical and accurate evaluation of this preparation process depending upon several factors [11, 13]. The factors studied here were Bi, Pb, Sr, Ca, and Cu content, heating-up time t_h (from the room temperature to annealing temperature), annealing temperature T_a, annealing time t_a, and the ambient to which samples were quenched after annealing *Q*. The prepared films were characterized structurally, morphologically, chemically, electrically and magnetically in order to evaluate results of a such statistic experimental design.

2. Experimental details

Bi-Pb-Sr-Ca-Cu-O film precursors were prepared by deposition of an aerosol from aqueous nitrate solutions on MgO substrates. Following our experimental design we investigated an influence of nine different variables upon synthesis of high-T_c phases, Table 1. The variation in the factors at two levels (low-high and/or min-max) was as follows: Bi in the mole number n_{Bi} = 1.65 and 2.09; Pb in the mole number n_{Pb} = 0.22 and 0.44; Sr in the mole number n_{Sr} = 1.98 and 2.42; Ca in the mole number n_{Ca} = 1.98 and 2.42; Cu in the mole number n_{Cu} = 2.75 and 3.85; heating-up time t_h = 0.5 and 1 h; annealing temperature T_a= 855 and 859ºC; annealing time t_a= 10 and 15 h; and the ambient into which samples were quenched after annealing *Q* = air and liquid nitrogen. To deposit the precursor films, a spray pyrolysis technique[12] has been applied using an ultrasonic generator to nebulize an aerosol. Basic initial solutions of Bi, Pb, Sr, Ca and Cu nitrates were prepared by dissolving appropriate amounts of $Bi(NO_3)_3$, $Pb(NO_3)_2$, $Sr(NO_3)_2$, $Ca(NO_3)_2.4H_2O$, and $Cu(NO_3)_2.3H_2O$ in deionized water. Solutions of the metal ions in the corresponding nominal composition, Table 1, were obtained by mixing the appropriate volumes of basic initial nitrate solutions. By means of the air as a carrier gas, the nebulized solutions of 0.02 molarity were sprayed over single crystal MgO (001) substrate preheated to 250ºC. The distance between the nozzle orifice and the substrate was kept at about 5 cm. The resulting precursor films, 5-10 μm thick, were then annealed in a tube-type furnace in air. The thermal treatment parameters of each sample were varied following the experimental design mentioned above. Sixteen various film-processing procedures were performed and the annealed films were then characterized in order to correlate their real properties with the design parameters. In order to verify results from the experimental design we prepared one last and modified trial numbered 17, Table 1, in which we used a substantially increased amount of Pb in comparison with the experimental design analysis. The synthesized film structure was studied by X-ray diffraction on a D-500 Siemens Diffractometer in the Bragg-Brentano (θ-2θ) geometry, using CuK_α radiation at 30kV and 20 mA. The surface morphology was examined by using the JEOL model 35 CF scanning electron microscope. Its energy-dispersive spectroscopy (EDS) attachment was used to analyze the chemical composition of the synthesized films. Magnetic moment vs temperature measurements with a magnetic field parallel and perpendicular to the sample surface were used to determine the critical temperature $T_{c,on}$ (onset) values. The T_c values of some samples were measured also by a standard transport current 4-point method, with the 1 μV/cm criteria.

Table 1. Parameters used to prepare Bi-Pb-Sr-Ca-Cu-O films, where n_{Bi}, n_{Pb}, n_{Sr}, n_{Ca}, n_{Cu} are the nominal amount of moles of Bi, Pb, Sr, Ca and Cu elements in the source solution, t_h is the heating-up time from room temperature to annealing temperature, T_a is the annealing temperature, t_a is the annealing time, and *Q* is the ambient into which samples were quenched after the annealing. Sample No. 17 was cooled down to the room temperature during 2 hours.

Trial No.	**Parameters of the film preparation**								
	n_{Bi}	n_{Sr}	n_{Pb}	n_{Cu}	n_{Ca}	T_a (°C)	t_a (h)	t_h (h)	*Q*
1	**1.65**	**1.98**	**0.22**	**2.75**	**1.98**	**855**	**10**	**0.5**	**Air**
2	2.09	1.98	0.22	2.75	2.42	855	15	1	$N_{2,liq}$
3	**1.65**	**2.42**	**0.22**	**2.75**	**2.42**	**859**	**10**	**1**	$\mathbf{N_{2,liq}}$
4	2.09	2.42	0.22	2.75	1.98	859	15	0.5	Air
5	**1.65**	**1.98**	**0.44**	**2.75**	**2.42**	**859**	**15**	**0.5**	$\mathbf{N_{2,liq}}$
6	2.09	1.98	0.44	2.75	1.98	859	10	1	Air
7	**1.65**	**2.42**	**0.44**	**2.75**	**1.98**	**855**	**15**	**1**	**Air**
8	2.09	2.42	0.44	2.75	2.42	855	10	0.5	$N_{2,liq}$
9	**1.65**	**1.98**	**0.22**	**3.85**	**1.98**	**859**	**15**	**1**	$\mathbf{N_{2,liq}}$
10	2.09	1.98	0.22	3.85	2.42	859	10	0.5	Air
11	**1.65**	**2.42**	**0.22**	**3.85**	**2.42**	**855**	**15**	**0.5**	**Air**
12	2.09	2.42	0.22	3.85	1.98	855	10	1	$N_{2,liq}$
13	**1.65**	**1.98**	**0.44**	**3.85**	**2.42**	**855**	**10**	**1**	**Air**
14	2.09	1.98	0.44	3.85	1.98	855	15	0.5	$N_{2,liq}$
15	**1.65**	**2.42**	**0.44**	**3.85**	**1.98**	**859**	**10**	**0.5**	$\mathbf{N_{2,liq}}$
16	2.09	2.42	0.44	3.85	2.42	859	15	1	Air
17	**1.65**	**2.42**	**1.8**	**3.85**	**2.42**	**859**	**15**	**2**	**Air**

3. Results and discussion

As an evaluation parameter of the quality of the prepared films we used the value $T_{c,on}$ which means in our case the onset on the measured magnetization curve, Table 2. The hypothesis of the experimental design assumes that the factors in the level that increases the $T_{c,\ average}$ ($T_{c,\ average}$ in the low or high level is calculated as an average of the $T_{c,on}$ values in the low or high level which for each factor are different and are fixed by the parameters of the experimental design) let us to improve the experimental $T_{c,on}$ in subsequent trials. The results of the experimental design analysis [13] suggested that, in order to improve the film $T_{c,on}$ values obtained in this study, the following values of factors must be used: n_{Bi} = 1.65; n_{Pb} = 0.44; n_{Sr} = 2.42; n_{Ca} = 1.98; n_{Cu} = 3.85; t_h = 1 h; T_a = 859ºC; t_a = 15 h; and *Q*= air, Fig. 1, which increased the $T_{c,\ average}$ values. In order to improve the $T_{c,on}$ values a trial numbered as 17, Table 1, was prepared and the results are also reported here.

X-ray patterns of the films prepared

Table 2. The critical temperature $T_{c,on}$ values obtained from magnetization measurements. Samples of trials No. 8, 10, 12 and 14 were not superconducting.

Trial No.	$T_{c,on}$ (K)
1	**85.5**
2	**88.0**
3	**77.5**
4	**82.5**
5	**84.0**
6	**85.5**
7	**88.0**
8	-
9	**86.0**
10	-
11	**85.5**
12	-
13	**87.0**
14	-
15	**86.0**
16	**90.0**

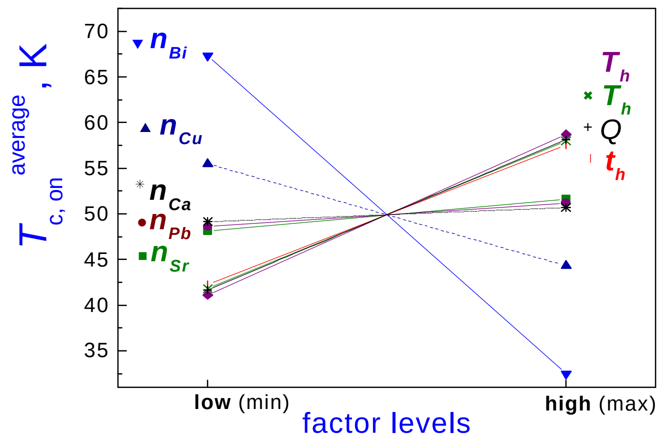

Fig. 1. Influence of parameters studied for two levels (min-max) of the fractional factorial experimental design 2_{III}^{9-5}. Left points in each line represent the minimum values used, and the right ones represent the maximum values.

following the experimental conditions No. 1, 11, and 16, Fig. 2, show increased amount of two high T_c superconducting phases namely $Bi_2Sr_2CaCu_2O_8$ (Bi-2212 phase) and that of $Bi_2Sr_2Ca_2Cu_3O_x$ (Bi-2223 phase) with the Bi content constant at its low level. The thermal treatment parameters varied in this case according to the experimental conditions No. 1, 11, and 16. In the Fig. 2(a), trial No. 1, the presence of the Bi-2212 phase can be observed. It seems that the nominal composition of the solution conditions $Bi_{1.65}Pb_{0.22}Sr_{1.98}Ca_{1.98}Cu_{2.75}O_x$ and the thermal treatment conditions being t_h = 30 min, T_a = 855ºC, t_a = 10 h followed by quenching in air are suitable for growing a film with and elevated amount of the Bi-2212 phase. Fig. 2 (b), trial No. 11, shows the presence of both, Bi-2212 and Bi-2223 phases. An increase in the Cu content from n_{Cu} = 2.5 to n_{Cu} = 3.5 and annealing time from 10 to 15 h enables a growth of the Bi-2223 phase. The X-ray pattern 2 (c), trial No. 16, shows the presence of the

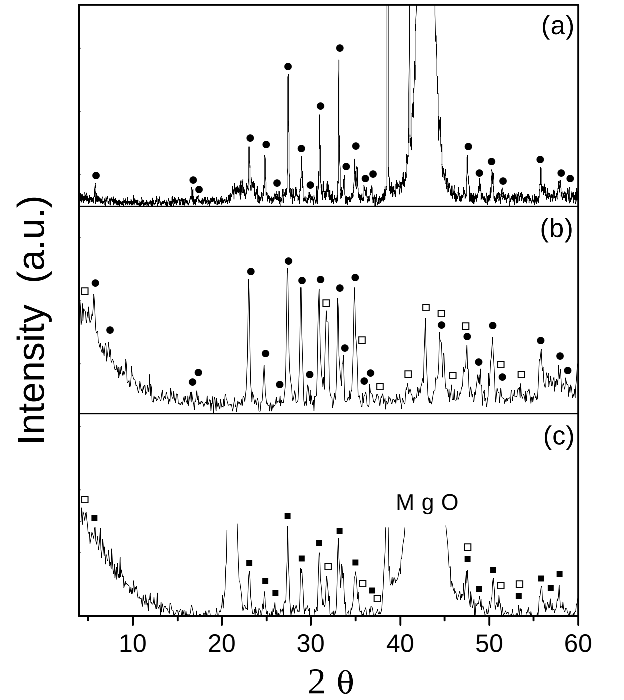

Fig. 2. X-ray diffraction patterns for Bi-Pb-Sr-Ca-Cu-O/MgO films prepared following the experimental conditions of trials No. 1 (a), No.11 (b), and No. 16 (c), Table 1. The detected phases are: ● $Bi_2Sr_2CaCu_2O_8$, □ $Bi_2Sr_2Ca_2Cu_3O_x$ and ■ $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_x$.

Bi-2223 and (Bi-Pb)-2223 phases obtained when annealing temperature and Cu cation content increase from 855 to 859ºC and/or from 2.75 to 3.85 respectively. We can see that annealing parameters and Cu content at their maximum levels and Bi content on its minimum level allow growth of the Bi-2223 phases. These results show that when the Bi content is used at its minimum value, i.e. n_{Bi} = 1.6, and the thermal treatment is also used at its maximum value, besides the 2212 phase, the initial growth of the 2223 phase may be observed. On the other hand, the X-ray pattern in Fig. 3 shows a negative influence of high level of the Bi content and low level of the thermal treatment parameters upon formation of superconducting phases. Fig. 3(a) shows the x-ray pattern of the film of the trial No. 10, where we can see that Bi with a cation content 2.09 (high level), annealing time of 10 h (low level), annealing temperature of 859ºC (high level) and heating-up time 0.5 h (low level), produce an oriented Bi-2201 phase (not superconducting above 10 K). Fig. 3(b) shows the x-ray pattern for the film of trial No. 14, where we can see the presence of the Bi_2SrO_4 not superconducting phase obtained when the annealing temperature is reduced to 855ºC and the Bi cation content is 2.09. The XRD measurements show both, the positive and negative effects of the film initial nominal composition mainly that of the Bi content in the low level and Cu in the high level together with the combination of annealing parameters. Apparently an important interaction between the Bi content

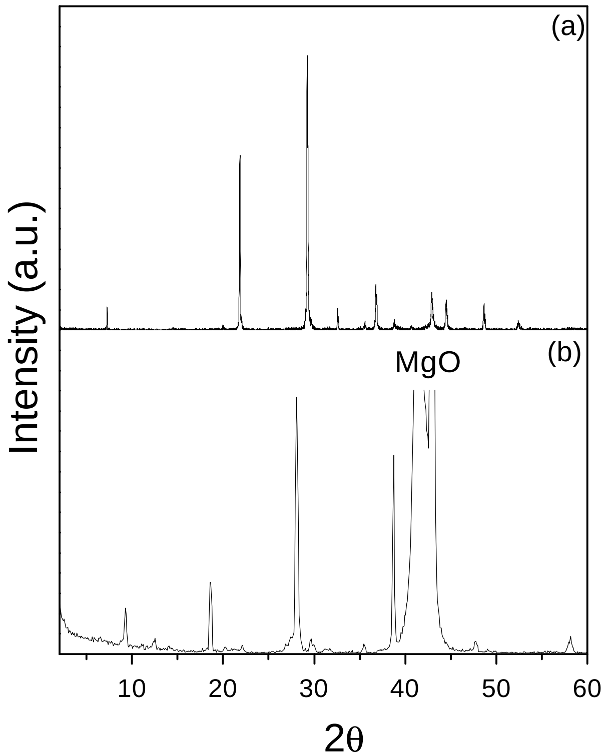

Fig. 3. X-ray diffraction patterns for Bi-Pb-Sr-Ca-Cu-O/MgO films prepared following the experimental conditions of trials No. 10 (a) and No. 14 (b), Table 1. The detected phases are $Bi_2Sr_2CuO_6$ and Bi_2SrO_4.

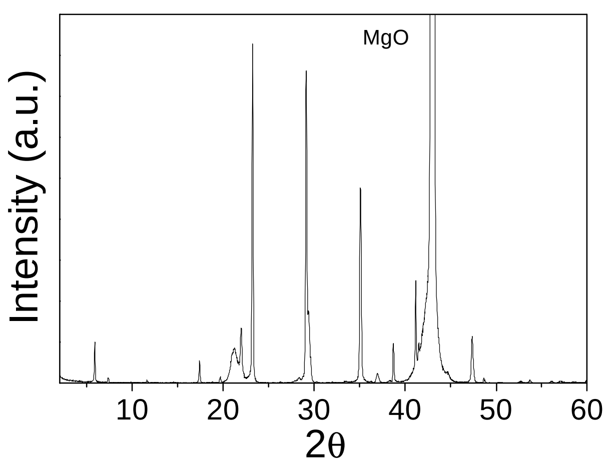

Fig. 4. X-ray diffraction pattern of Bi-Pb-Sr-Ca-Cu-O/MgO film prepared following the experimental conditions of trial No. 17, Table 1. The detected phases are: $Bi_2S_2Ca_2Cu_4O_x$, and $Bi_2Sr_2CuO_6$.

and the film heat treatment conditions exists, since the formation of superconducting phases depends upon Bi content in the low level and annealing conditions in the high level. In the opposite case, high Bi content and low annealing conditions produce loss of the Bi-2212 and Bi-2223 phases. These results are in agreement with those reported in references [5,14,15]. Fig. 4 shows the X-ray pattern of the film prepared following the conditions of trial No. 17 which represents the best preparation conditions studied here, giving the highest T_c value. Formation of the 00*l*-oriented Bi-2224 phase may also be seen.

Fig. 5(a) shows a surface morphology obtained with backscattered electrons from the film of the trial No. 11, which consists mainly of plate-like crystal grains oriented parallel with the film surface, with the real film composition $Bi_{1.65}Sr_{1.65}Ca_{1.3}Cu_{2.8}O_x$. Irregular dark particles of the $SrCaCu_4$ composition may also be observed. All the films presented Pb deficiency due to its partial evaporation during an annealing. Fig. 5(b) shows the film surface morphology (obtained by means of backscattered electrons) of the film of trial No. 16, which also consists mainly of plate-like grains oriented parallel to the film surface with the real composition $Bi_{1.65}Pb_{0.08}Sr_{1.54}Ca_{1.73}Cu_{1.56}O_x$. The irregular dark particles consist of Sr-Ca-Cu-O phase rich in Sr. From those pictures, following the processing conditions, we can observe that both, annealing time and the annealing temperature have a pronounced influence on the particle size. The size of grains increases with annealing time and temperature [12]. However, the EDS analyses suggest a strong loss of the Pb component in the films, which means

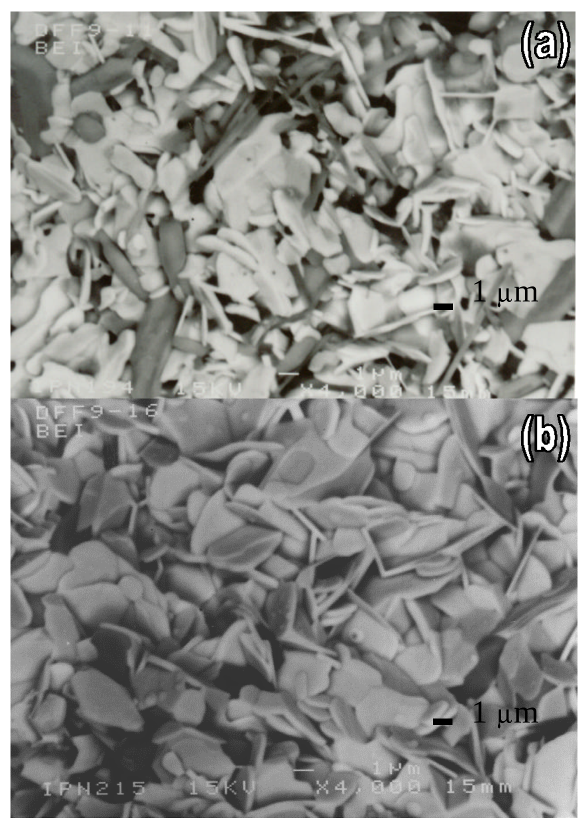

Fig. 5. Surface morphology obtained with backscattered electrons for Bi-Pb-Sr-Ca-Cu-O/MgO films prepared following the experimental conditions of trials No. 11 (a) and 16 (b), Table 1.

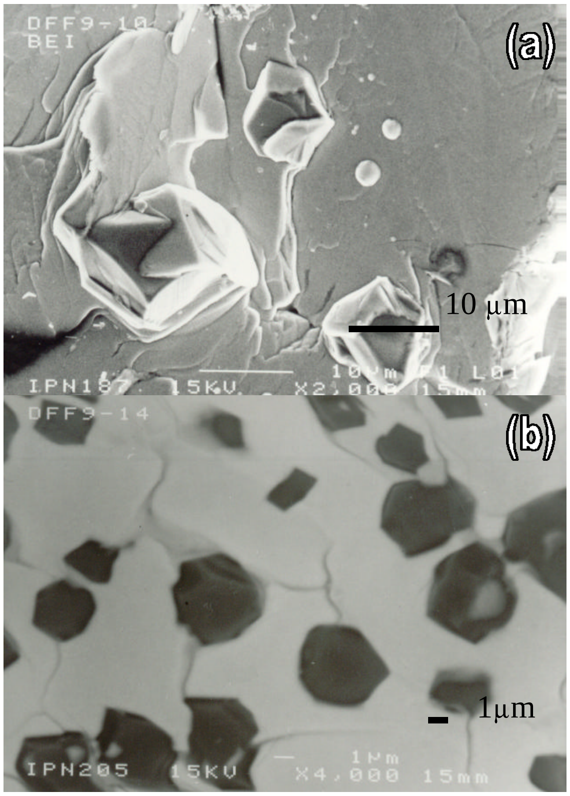

Fig. 6. Surface morphology obtained with backscattered electrons for Bi-Pb-Sr-Ca-Cu-O/MgO films prepared following the experimental conditions of trials No. 10 (a) and No. 14 (b), Table 1.

a necessity to increase the initial amount of Pb to show the effect upon the growth of superconducting phases, trial No. 17. Fig. 6(a) shows surface morphology obtained with backscattered electrons from the film of trial No. 10. We can see dark particles of Cu arising from a melted material of composition $Bi_2Pb_{0.15}Sr_{1.4}Ca_{0.7}Cu_{1.4}O_x$. Fig. 6(b) reveals the surface morphology obtained also by means of backscattered electrons from the film of trial No. 14. Here we may observe round dark particles of the composition $Bi_{1.2}Sr_{1.4}Ca_{0.4}Cu_{0.1}O_x$ arising from the well-oriented plate-like grains of the composition $Bi_2Sr_1Ca_{0.4}Cu_{0.1}O_x$. The SEM investigations allow us to observe that the conditions where Bi is maintained at cation content 1.65, in combination with the annealing conditions kept on their high level, enable growth of plate-like grains oriented parallel with the substrate surface. According to the XRD analysis, the grain phase composition correspond mainly to the Bi-2212 and Bi-2223 phases which is in an agreement also with the EDS analysis. When maximum values of annealing parameters and maximum Bi content are used, the material is melted and phases without presence of calcium are formed. Particles then appear rich in strontium and calcium without presence of copper.

Fig. 7 shows the magnetic moment vs temperature dependence of several films prepared following experimental conditions No. 1, 11 and 16, obtained with the magnetic field parallel to the film surface. All the films

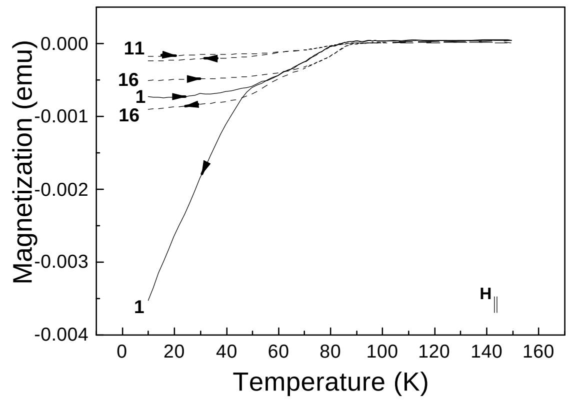

Fig. 7. The magnetization vs. temperature dependence for Bi-Pb-Sr-Ca-Cu-O/MgO films prepared following the experimental conditions of trials No. 1, 11 and 16. The magnetic field was oriented parallel to the film surface. The intensity of magnetic field was 100 Oe (- - -) and 1000 Oe (——).

prepared with the Bi content on its low level were superconducting. Films prepared with the maximum Bi content either did not present any superconducting transition, or presented very low $T_{c,on}$ values only. The magnetization curves of all the measured films were similar. Results of the $T_{c,on}$ measurements show that, in order to obtain higher $T_{c,on}$ values, it is necessary to keep the Bi content on its minimum value, n_{Bi} = 1.65, and the heat processing parameters on their maximum values, i.e. T_a = 859ºC and t_a = 15 h.

Fig. 8 shows the resistance vs. temperature dependence of films of trials No. 11 and 17, Table 1. Here we observe semiconducting behavior of film No. 11, two transitions at 96 and 68 K, and a T_c *(R = 0)* = 37 K. The dependence for the film of trial No. 17 prepared with a substantially increased amount of lead is also shown in Fig. 8. Here we can see a metallic behavior, two transitions at 105 and 84 K, and a T_c *(R = 0)* = 73 K. Results of the Fig. 8 show the usefulness of our experimental procedure and its systematic approach with the aim to obtain superconducting samples with higher critical temperature T_c values.

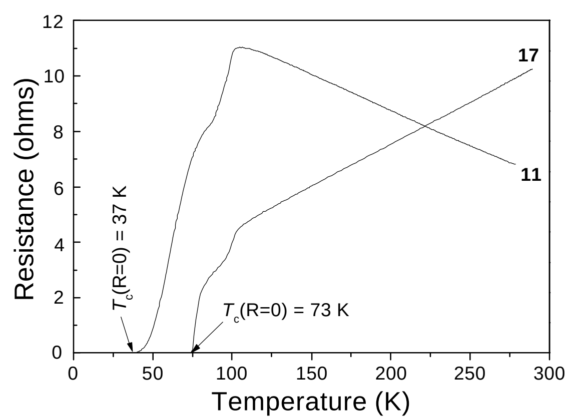

Fig. 8. The resistance vs. temperature dependence for Bi-Pb-Sr-Ca-Cu-O/MgO films prepared following the experimental conditions of trials No. 11 and No. 17, Table 1.

4. Conclusions

Films of 5-10 μm in thickness were prepared by spray pyrolysis technique according to a fractional factorial experimental design. Results of the analyses of the experimental design and those obtained from characterizations (XRD, SEM, EDS and the critical temperature value measurements) showed that the variables with the highest influence upon the growth of high-T_c superconducting phases are Bi content, annealing time and temperature, and the quenching ambient. The results suggest a use of the value of 1.65 (low level) as a mole content of Bi, thermal treatment conditions in their high level values, i.e 1 h, 859ºC, 15 h, and air as a quenching ambient for t_h, T_a, t_a and Q respectively, to obtain superconducting BSCCO films with improved properties. On the other hand, we can see that the change in Sr and Ca content have lower influence upon improving of superconducting properties when their mole content is between 1.98 an 2.42. An evident loss of Pb was observed during the whole experimental work caused by its partial evaporation. The most important improvement in T_c values was obtained by utilizing the nominal content of n_{Bi} = 1.65, n_{Cu} = 3.85, n_{Sr} = 2.42, n_{Ca} = 2.42 with a substantial increase in the Pb content from the nominal value n_{Pb} = 0.44 to n_{Pb} = 1.8 in deposited precursor films, annealed under the conditions of annealing temperature T_a = 859°C, annealing time of t_a =15 h, heating-up temperature t_h = 2 h and cooling down in air to room temperature during 2 hours.

Acknowledgments

The authors acknowledge the technical assistance of J. García-Coronel and M. Guerrero-Cruz. CEGEPI-IPN Proyect No. 980250 supported the work.

References

[1]. H. Maeda, Y. Tanaka, M. Fukutomi, and T Asano, Jpn. J. Appl. Phys., **27**, L209-L210(1988).
[2]. M. Takano, J. Takada, K. Oda, H. Kitaguchi, Y. Miura, Y. Ikeda, Y. Tomii, and H. Mazaki, Jpn. J. Appl. Phys. **27**, L1041-L1043(1988).
[3]. E. Díaz-Valdés, G. Pacheco-Malagón, G. Contreras-Puente, C. Mejía-García, G. Andrade-Garay and J. Ortíz-López, A. Conde-Gallardo and C. Falcony, Materials Chemistry and Physics, **36**, 64-67(1993).
[4]. K. Ikeda, K. Gotoh, M. Ihara, and M. Ozeki, Jpn. J. Appl. Phys. **28**, L650-L652(1989).
[5]. K. Ohbayashi, M. Anma, Y. Takai, and H. Hayakawa, Jpn. J. Appl. Phys. **29**, L2049(1990).
[6]. W. Kula, R. Sobolewski, J. Górecka, and S. J. Lewandowski, J. Appl. Phys. **70**, 3171(1991).
[7]. N. Takahashi, A. Koikitu, H. Seki, and Y. Kamioka, J. Crystal Growth **144**, 48(1994).
[8]. H. Nobumasa, K. Simizu, Y. Kitano, and T. Kawai, Jpn. J. Appl. Phys. **27**, L1669(1988).
[9]. H. S. Koo, G. C. Tu, J. J. Chu, W. H. Lee, and P. T. Wu, J. Mat. Sc. Lett. **9**, 1326-1328(1990).
[10]. R. G. Buckley, J. L. Tallon, I. W. M. Brown, M. R. Presland, N. E. Flower, P. W. Gilberd, M. Bowden and N. B. Milestone, Physica C 156, 629(1988).
[11]. D. C. Montgomery, *Design and Analysis of Experiments*, 1st ed. Wiley, New York, 239-235 (1976).
[12]. M. Jergel, F. Hanic, V. Strbik, J. Liday, G. Plesch, T. Melisek, and M. Kubranová, Supercond. Sci. Technol. **5**, 663(1992).
[13]. E. Díaz *et. al.*, "Application of the fractional factorial experimental design in the preparation of superconducting thin films" , *to be published.*
[14]. H. M. Hsu, I. Yee, J. Deluca, C. Hilbert, R. F. Miracky, and L. N. Smith, Appl. Phys. Lett. **54**, 957(1989).
[15]. H. S. Koo, G. C. Tu, J. J. Chu, W. H. Lee, and P. T. Wu, J. Mat. Sc. Lett. **9**, 1326(1990).